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<p>(21) International Application Number: PCT/AU87/00396</p> <p>(22) International Filing Date: 25 November 1987 (25.11.87)</p> <p>(31) Priority Application Number: PH 9148</p> <p>(32) Priority Date: 25 November 1986 (25.11.86)</p> <p>(33) Priority Country: AU</p> <p>(71) Applicant (for all designated States except US): COMMONWEALTH SCIENTIFIC AND INDUSTRIAL RESEARCH ORGANISATION [AU/AU]; Lime-stone Avenue, Campbell, ACT 2601 (AU).</p> <p>(72) Inventors; and</p> <p>(75) Inventors/Applicants (for US only) : ROTHSCHILD, George, Heinrich, Ludwig [AU/AU]; Gwaiwunda, Yass River Road, Gundaroo, NSW 2620 (AU). WHITTLE, Christopher, Playford [AU/AU]; 9 Whitham Place, Pearce, ACT 2607 (AU). BELLAS, Thomas, Edward [AU/AU]; 6 Coates Place, Weston, ACT 2611 (AU). VICKERS, Richard, Alan [AU/AU]; 17 Beaurepaire Crescent, Holt, ACT 2615 (AU).</p>	<p>(74) Agents: SLATTERY, John, Michael et al.; Davies & Collison, 1 Little Collins Street, Melbourne, VIC 3000 (AU).</p> <p>(81) Designated States: AT (European patent), AU, BE (European patent), CH (European patent), DE (European patent), FR (European patent), GB (European patent), IT (European patent), LU (European patent), NL (European patent), SE (European patent), US.</p> <p>Published With international search report. With amended claims.</p>	
<p>(54) Title: IMPROVED PHEROMONE FORMULATION</p> <p>(57) Abstract</p> <p>A synthetic pheromone composition for use in the control of the codling moth (<i>Cydia pomonella</i>), in a crop or orchard, comprises: (1) <i>trans, trans</i> - 8,10,dodecadien-1-ol, (2) at least one additional component selected from dodecanol and/or tetradecanol, and, optionally, (3) a carrier material or substance therefor.</p>		

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"IMPROVED PHEROMONE FORMULATION"

This invention relates to an improvement in the formulation of a synthetic sex pheromone composition used for the control of the codling moth (Cydia pomonella), a major pest of apples and pears, by means of mating
5 disruption.

Pheromones are chemicals secreted by an insect to affect the behaviour of other insects of the same species. Pheromones have been used in a number of biological pest control methods, and the use of these
10 natural substances is attractive because of the high selectivity of these substances, combined with the fact that insects may be less likely to develop a resistance to them than, for example, to synthetic organic insecticides.

Sex pheromones, and particularly female sex
15 pheromones, have been used for some time in insect control methods, and in one such method the female sex pheromone is used as "bait" in traps used to attract and catch male insects. In another such method, the female sex pheromone

is evaporated from a number of sources to confuse the male insects and frustrate their attempts to locate females, hence disrupting mating.

5 Previous approaches to control codling moth by mating disruption have been based on the use of a single synthetic compound, trans,trans-8,10, dodecadien-1-ol (E,E,8,10-12OH), which is known to be the major component of the natural sex pheromone of the female codling moth. However, treatments with synthetic E,E,8,10-12OH have
10 provided very variable results in terms of levels of codling moth damage to fruit such as apples or pears, although the single component generally reduces the number of male codling moths locating virgin female or synthetic pheromone sources.

15 It has now been discovered that the natural sex pheromone of codling moth females contains several other components in addition to E,E,8,10-12OH which, when formulated with synthetic E,E,8,10-12OH, provide a synthetic pheromone composition that is significantly more
20 effective than E,E,8,10-12OH alone in mating disruption trials in codling moth, both in reducing male captures at synthetic pheromone sources and in terms of reduced fruit damage.

According to a first aspect of the present invention, there is provided a synthetic pheromone
25 composition for use in the control of the codling moth (Cydia pomonella), which comprises (1) trans, trans-8,10, dodecadien -1-ol, (2) at least one additional component selected from dodecanol and/or tetradecanol, and, optionally (3) a carrier material or substance therefor.
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In another aspect, the present invention provides a method for the control of the codling moth (Cydia pomonella) in a crop or orchard, which comprises the step of releasing in the crop or orchard an effective amount of
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a composition comprising (1) trans, trans-8,10, dodecadien-1-ol, and (2) at least one additional component selected from dodecanol and/or tetradecanol, and, optionally (3) a carrier material or substance therefor.

5 The amount of the composition of this invention which is effective in the control of the codling moth by mating disruption can, of course, be readily determined by simple field trials. By way of example, however, the release of the composition at a rate to maintain the
10 active components at or above 25mg per hectare of crop or orchard treated per hour, has been found to be effective. A preferred rate of release is about 35 mg per hectare treated per hour.

15 Preferably, the composition of this invention comprises the three active components, E,E,8,10-12OH (component I), dodecanol (component II) and tetradecanol (component III).

20 As previously described, the composition optionally includes a carrier material or substance. One suitable carrier material is octanol, which may be included in the composition in order to reduce the melting point of the active components.

25 The composition may also contain an antioxidant, such as alpha-tocopherol, which may be used in an amount of approximately 10% by weight of the total composition.

30 Preferably also, the composition of this invention is provided in and released from vapor-releasing dispensers which can be distributed at appropriate points throughout the crop or orchard to be treated. Suitable dispensers include the polymeric tubular vapor-releasing dispensers having shape retainability disclosed in
Australian Patent Specification No.534,192.

4 Preferably also, the ratios of the three components, released from vapor-releasing dispensers, are

1.0:0.5:0.1 for components I, II and III, respectively. As described above, the combined mean release rate for the three components over the season is preferably maintained at or above 25mg per hectare per hour - for example, using
5 1000 polymeric tubular vapor-releasing dispensers, each loaded with ca. 80mg, per hectare. The number of dispensers per hectare can, of course, be varied provided that the overall release rate is maintained at an appropriate level.

10 Whilst the preferred ratios of the three components for biological effectiveness are as described above, the dodecanol and/or tetradecanol may be included in the initial composition in amounts which exceed the optimum for biological effectiveness. This is to
15 counteract the effect of differences between the initial composition and effluvia when dispensed, for example by permeation from a dispenser such as the capillary dispenser of Australian Patent Specification No.534,192.

20 Further features of the present invention will be apparent from the following Examples, included by way of illustration of the invention.

Example 1

In a field trial comparing the effectiveness of the single component (A) versus the 3-component blend (B) and untreated control (C), each of the trial compositions
25 was released from polymeric tubular dispensers as described in Australian Patent Specification No.534,192. The level of fruit damage in (B) was significantly lower (<0% fruit damaged) than (A) or (C) which exceeded 19% and 80% respectively. Mean male codling moth captures per
30 pheromone baited trap over a three month period in (B), (A) and (C) were 0, 6 and 28, respectively. The 3-component blend in accordance with the present invention was therefore significantly more effective than either the

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single component or the control, both in reducing fruit damage and in reducing male captures at the synthetic pheromone sources.

5 The field results were supported by laboratory bioassays in which the sexual activity of male codling moths was measured in response to trans, trans-8, 10, dodecadien-1-ol (I) alone or in combination with dodecanol (II) and tetradecanol (III). The percent response was as follows I alone -27%, I plus II-22%, I plus III-23%, I plus II and III-63%. There was no response to the control (clean air).

10 Example 2

A three component pheromone blend in a slow release dispenser was trialled at commercial pear orchards in the Goulburn Valley in Victoria, Australia.

15 The Trial Design

Each trial consisted of a paired comparison between a conventionally treated orchard and a pheromone treated orchard. An adjoining block of pears of the same variety but with conventional spray programme was monitored as the control at each site. The trial sites were not well isolated (desirable for pheromone trials) but where pheromone and conventionally treated orchards adjoined each other, the pheromone dispensers were placed in 6 rows of the conventionally treated orchard to provide a buffer zone of an effectively doubly treated area. A conventional fungicide programme was maintained on both test and control orchards.

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a. Pheromone dispenser design

The pheromone mixture consisted of a blend of three components as follows:

	<u>Compound</u>	<u>Proportion</u>
5	E,E,8,10-12OH	1000
	Dodecanol	500
	Tetradecanol	100

The above mixture was combined in a 90:10 w/w ratio with alpha tocopherol as an antioxidant, drawn into the capillary dispenser tube under vacuum and sealed and guillotined into 200 mm lengths. The dispensers were constructed in accordance with Australian Patent Specification No.534,192 and were comprised of a blend of polyethylene and ethylene/vinyl alcohol which allows the pheromone to release by slow permeation of the dispenser walls. A soft aluminium wire was incorporated into the dispenser beside the capillary to facilitate attachment to the branches of the trees. The capillary lumen was 2 mm and the capillary wall thickness was 0.5 mm.

b. Spray Programmes - Control orchards:

	<u>Insecticide</u>	<u>No. of Applications</u>	
		Site 1	Site 2
	Chlorpyrifos	-	1
25	Azinphos methyl	-	3
	Parathion	10	1
	<u>Bacillus thuringiensis</u>	2	3

c. Dispenser placement

The dispensers were placed 4 per tree at a height of approximately 2 metres on the perimeter branches of the trees. This gave an overall density of 1000 dispensers per hectare. The dispensers were placed in the field at a date estimated to be one to two weeks prior to Coding moth emergence based on previous years experience.

d. Monitoring

All the treatment and control areas were monitored using Terpinyl acetate/sugar lures and pheromone traps. Coding moth damage was assessed at harvest.

5 e. Results

Coding moth populations were low, as expected in a normal commercially run orchard.

Coding Moth Damage

10	Site	Treatment	No. of fruit checked	No. of fruit infested	Damage %
	1	Control	600	1	0.5
		Test	400	0	0
15	2	Control	500	2	0.4
		Test	1000	3	0.3

20 It will be appreciated that modifications and variations may be made to the particular embodiments specifically described without departing from the broad concepts of this invention as described herein, and that the present invention extends to all such modifications and variations which fall within the spirit and scope of

25 the invention.

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CLAIMS

1. A synthetic pheromone composition for use in the control of the codling moth (Cydia pomonella), which comprises:
 - (1) trans, trans - 8, 10, dodecadien-1-ol,
 - (2) at least one additional component selected from dodecanol and/or tetradecanol, and, optionally
 - (3) a carrier material or substance therefor.
2. A composition according to claim 1, comprising trans, trans - 8, 10, dodecadien-1-ol, dodecanol and tetradecanol.
3. A composition according to claim 2, wherein said components are in the ratio of 1.0 : 0.5 : 0.1, respectively.
4. A composition according to claim 1, further comprising an antioxidant.
5. A composition according to claim 4, wherein said antioxidant is alpha-tocopherol.
6. A composition according to claim 1, further comprising octanol.
7. A composition according to any one of claims 1 to 6, wherein said components are contained within a tubular polymeric vapor-releasing dispenser.
8. A method for the control of the codling moth (Cydia pomonella) in a crop or orchard, which comprises the steps of releasing in the crop or orchard an effective

amount of a composition according to any one of claims 1 to 7.

9. A method according to claim 8, wherein said composition is released at a rate effective to maintain the active components at or above 25 mg per hectare per hour.

10. A method according to claim 9, wherein said composition is released at a rate effective to maintain the active components at about 35 mg per hectare per hour.

AMENDED CLAIMS

[received by the International Bureau
on 9 May 1988 (09.05.88);
claim 2 cancelled; claims 1 and 3 amended;
other claims unchanged (1 page)]

1. (Amended) A synthetic pheromone composition for use in the control of the codling moth (Cydia pomonella), which comprises:
 - (1) trans, trans - 8, 10, dodecadien-1-ol,
 - (2) dodecanol,
 - (3) tetradecanol, and, optionally,
 - (4) a carrier material or substance therefor.
2. (Cancelled)
3. (Amended) A composition according to claim 1, wherein said components are in the ratio of 1.0 : 0.5 : 0.1, respectively.
4. A composition according to claim 1, further comprising an antioxidant.
5. A composition according to claim 4, wherein said antioxidant is alpha-tocopherol.
6. A composition according to claim 1, further comprising octanol.
7. A composition according to any one of claims 1 to 6, wherein said components are contained within a tubular polymeric vapor-releasing dispenser.
8. A method for the control of the codling moth (Cydia pomonella) in a crop or orchard, which comprises the steps of releasing in the crop or orchard an effective

INTERNATIONAL SEARCH REPORT

International Application No. PCT/AU 87/00396

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all.) According to International Patent Classification (IPC) or to both National Classification and IPC <div style="display: flex; justify-content: space-between; margin-top: 5px;"> Int. Cl.⁴ A01N 31/02 </div>																
II. FIELDS SEARCHED <div style="display: flex; justify-content: space-between; margin-top: 5px;"> Classification System Minimum Documentation Searched¹ </div> <div style="display: flex; justify-content: space-between; margin-top: 10px;"> IPC A01N 31/02, 9/24 </div> <div style="margin-top: 10px;"> Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched¹ </div> <div style="margin-top: 10px;"> AU : IPC as above </div>																
III. DOCUMENTS CONSIDERED TO BE RELEVANT² <table style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th style="width: 5%; text-align: left; border-bottom: 1px solid black;">Category³</th> <th style="width: 85%; text-align: left; border-bottom: 1px solid black;">Citation of Document,¹¹ with indication, where appropriate, of the relevant passages¹²</th> <th style="width: 10%; text-align: left; border-bottom: 1px solid black;">Relevant to Claim No.¹³</th> </tr> </thead> <tbody> <tr> <td style="vertical-align: top;">A</td> <td>AU,B, 461516 (28242/71) (COMEAU, Andre, ROELOFS, Wendell, HILL, Ada) 2 November 1972 (02.11.72)</td> <td style="vertical-align: top; text-align: center;">(1-10)</td> </tr> <tr> <td style="vertical-align: top;">A</td> <td>Journal of Chemical Ecology, Vol.8 No.2 (1982) p. 397-408, "Compounds Modifying the Activity of Two Sex Attractants for Males of the Pea Moth <i>Cydia nigricana</i> (F.)" (A.R. Greenway, C. Wall and J.N. Perry)</td> <td style="vertical-align: top; text-align: center;">(1-10)</td> </tr> <tr> <td style="vertical-align: top;">X</td> <td>Chemical Abstracts, Volume 104, no.23, issued 1986 June 9 (Columbus, Ohio, U.S.A.) Einhorn, J., et al. "Secondary components of the codling moth (<i>Cydia pomonella</i> L.) (Lepidoptera, Tortricidae) sex pheromone II. First results on the behavioral effects." see monograph 202262p, C.R. Acad. Sci., Ser. 3, 1986, 302(7), 263-6 (Fr.)</td> <td style="vertical-align: top; text-align: center;">(1-10)</td> </tr> <tr> <td style="vertical-align: top;">A</td> <td>Chemical Abstracts, Volume 102, no.15, issued 1985 April 15 (Columbus, Ohio U.S.A.) Einhorn, J., et al., "Secondary constituents of the codling moth (<i>Cydia pomonella</i> L.) (Lepidoptera, Tortricidae) sex pheromone" see monograph 129143c, C.R. Acad. Sci., Ser. 3, 1984, 299(19), 773-8 (Fr.)</td> <td style="vertical-align: top; text-align: center;">(1-10)</td> </tr> </tbody> </table>		Category ³	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³	A	AU,B, 461516 (28242/71) (COMEAU, Andre, ROELOFS, Wendell, HILL, Ada) 2 November 1972 (02.11.72)	(1-10)	A	Journal of Chemical Ecology, Vol.8 No.2 (1982) p. 397-408, "Compounds Modifying the Activity of Two Sex Attractants for Males of the Pea Moth <i>Cydia nigricana</i> (F.)" (A.R. Greenway, C. Wall and J.N. Perry)	(1-10)	X	Chemical Abstracts, Volume 104, no.23, issued 1986 June 9 (Columbus, Ohio, U.S.A.) Einhorn, J., et al. "Secondary components of the codling moth (<i>Cydia pomonella</i> L.) (Lepidoptera, Tortricidae) sex pheromone II. First results on the behavioral effects." see monograph 202262p, C.R. Acad. Sci., Ser. 3, 1986, 302(7), 263-6 (Fr.)	(1-10)	A	Chemical Abstracts, Volume 102, no.15, issued 1985 April 15 (Columbus, Ohio U.S.A.) Einhorn, J., et al., "Secondary constituents of the codling moth (<i>Cydia pomonella</i> L.) (Lepidoptera, Tortricidae) sex pheromone" see monograph 129143c, C.R. Acad. Sci., Ser. 3, 1984, 299(19), 773-8 (Fr.)	(1-10)
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(continued)																
<div style="display: flex; justify-content: space-between;"> <div style="width: 60%;"> <p>* Special categories of cited documents:¹⁰</p> <ul style="list-style-type: none"> - "A" document defining the general state of the art which is not considered to be of particular relevance - "E" earlier document but published on or after the international filing date - "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) - "O" document referring to an oral disclosure, use, exhibition or other means - "P" document published prior to the international filing date but later than the priority date claimed </div> <div style="width: 35%;"> <ul style="list-style-type: none"> - "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention - "X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step - "Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. - "Z" document member of the same patent family </div> </div>																
IV. CERTIFICATION <table style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 60%; vertical-align: top;"> Date of the Actual Completion of the International Search 4 March 1988 (04.03.88) </td> <td style="width: 40%; vertical-align: top;"> Date of Mailing of this International Search Report (14.03.88) 14 MARCH 1988 </td> </tr> <tr> <td style="vertical-align: top;"> International Searching Authority Australian Patent Office </td> <td style="vertical-align: top;"> Signature of Authorized Officer <div style="text-align: right;">C.A. BRICK</div> </td> </tr> </table>		Date of the Actual Completion of the International Search 4 March 1988 (04.03.88)	Date of Mailing of this International Search Report (14.03.88) 14 MARCH 1988	International Searching Authority Australian Patent Office	Signature of Authorized Officer <div style="text-align: right;">C.A. BRICK</div>											
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FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

- X Experimentia, Vol. 41 no. 11 (1985) 1482-4 (1-10)
 (Arn, H., Guerin, P.M. et al) "Sex pheromone
 blend of the codling moth Cydia pomonella :
 Evidence for a behavioral role of dodecan-1-ol"

V. OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE

This international search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1. ☐ Claim numbers because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claim numbers because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☐ Claim numbers because they are dependent claims and are not drafted in accordance with the second and third sentences of PCT Rule 6.4(e).

VI. OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING

This International Searching Authority found multiple inventions in this international application as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.
2. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:
3. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:
4. ☐ As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

Remarks on Protest

- ☐ The additional search fees were accompanied by applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.